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Compounds containing 3-metallated pyrrole [1]

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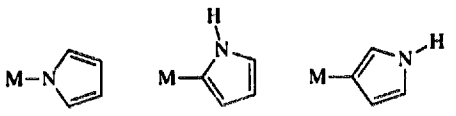
Abstract

In this paper we describe the synthesis of 3-metallated pyrroles where the pyrrole ring is otherwise unsubstituted at either carbon or nitrogen.

Keywords: Ruthenium; Pyrrole; Mercury

1. Introduction

There are essentially two different ways in which the pyrrolyl anion can interact with a metal centre. These can be described either as an idealized or distorted version of π-bonding or as a species with a σ-bond between the metal and one of the ring atoms. In this second category, compounds containing a nitrogen–metal bond (type I, see below) are well known. However, η^1-C bound pyrrolyl complexes of the type II were unknown until our initial report in 1989 [1] and few have been reported since then [2–4]. There appear to be no reports of simple 3-metallopyrroles (type III). Several examples of 2- or 3-metallopyrroles in which the pyrrole ring bears additional substituents on the nitrogen or carbon atoms are known; for example, see Ref. [5].



I II III

Following the successful synthesis of 2-metallated pyrrole derivatives [1,3,4] we turned our attention to the synthesis of a compound containing a 3-metallated pyrrole. The selectivity for attack of an electrophile like Hg^{2+} at the 2-position of pyrrole can be increased by substitution at the nitrogen atom with an electron withdrawing group [4]. In contrast, use of the bulky, electron-releasing triisopropylsilyl group as a nitrogen substituent has been reported to direct attack to the 3-position. Thus, bromination of *N*-(triisopropylsilyl)pyrrole with *N*-bromosuccinimide (NBS) gives 3-bromo-*N*-(triisopropylsilyl)pyrrole in nearly quantitative yield [6].

We now report the synthesis of the 3-mercurated pyrrole $(3\text{-}C_4H_3NSi[CH(CH_3)_2]_3)HgCl$ (1) from 3-bromo-*N*-(triisopropylsilyl)pyrrole using *n*-butyllithium and mercuric chloride (see Scheme 1).

2. Experimental and results

$(3\text{-}C_4H_3NSi[CH(CH_3)_2]_3)HgCl$ (1) was prepared in the following way: *n*-butyllithium in hexane (7 ml, 1.6 M) was transferred by cannula to a solution of 3-bromo-*N*-(triisopropylsilyl)pyrrole (3.4 g, 11.2 mmol) in 50 ml tetrahydrofuran at −100 °C. After 30 min at this temperature, a pre-cooled solution of mercuric chloride (3.05 g, 11.2 mmol) in tetrahydrofuran (30 ml) was added in the same way. The solution was allowed to warm to room temperature, and then triethylamine (2.3 ml) was added and the volume of the solution reduced. Recrystallization from dichloromethane–ethanol gave pure 1 (4.21 g, 82%). Data for 1: m.p. 128 °C; IR (nujol mull, cm^{-1}) 3090, 1560, 1260, 1220, 1200, 1082, 1015, 997, 959, 915, 884, 782, 715, 692, 659, 632, 614, 579, 525, 446, 342 (νHgCl), 323

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[1] Dedicated to Professor Dr. Max Herberhold on the occasion of his 60th birthday.

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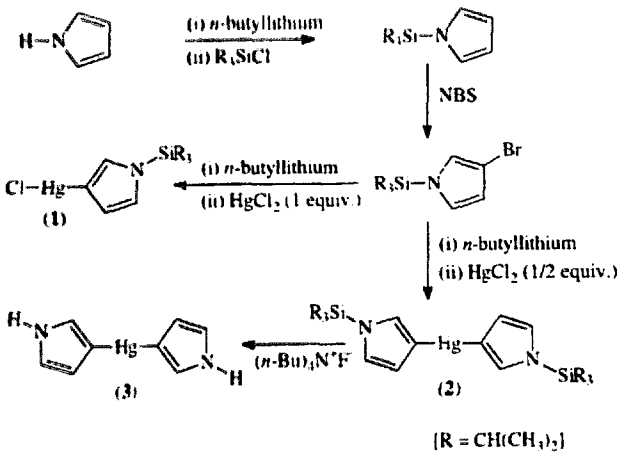


Scheme 1.

(νHgCl); ^{1}H NMR ($CDCl_3$, δ in ppm, J in Hz, TMS at $\delta = 0$) 6.99 (s, 1H, C*H*), 6.74 (s, 1H, C*H*), 6.31 (s, 1H, C*H*), 1.09 (d, 18H, $^3J_{HH} = 7.46$, Si[CH(CH_3)$_2$]$_3$), 1.46 (sept, 3H, $^3J_{HH} = 7.48$, Si[C*H*(CH$_3$)$_2$]$_3$). ^{13}C NMR ($CDCl_3$, δ in ppm, J in Hz, TMS at $\delta = 0$) 129.3 (s, *C*H, Hg-satellite: d, J_{CHg} 304.8), 124.4 (s, *C*H, Hg-satellite: d, J_{CHg} 211.3), 115.0 (s, *C*H, Hg-satellite: d, J_{CHg} 180.1), 17.7 (s, Si[CH(*C*H$_3$)$_2$]$_3$), 11.7 (s, Si[*C*H(CH$_3$)$_2$]$_3$), (quaternary carbon atom not observed). Anal. Found: C, 33.90; H, 5.01; N, 2.86. $C_{13}H_{24}ClHgNSi$. Calc: C, 34.06; H, 5.28; N, 3.06%. MS: m/z 459 (M^+).

Using only half an equivalent of mercuric chloride leads predominantly to the symmetric organomercury compound, (3-$C_4H_3NSi[CH(CH_3)_2]_3)_2Hg$ (**2**). Pure samples of this product can be obtained in ca. 64% yield after recrystallization to remove small amounts of **1** (ca. 5%).

(3-$C_4H_3NSi[CH(CH_3)_2]_3)_2Hg$ (**2**) was prepared as described for **1** above, but with only one-half an equivalent of mercuric chloride (3.4 g 3-bromo-*N*-(triisopropyl-silyl)pyrrole needs 1.52 g (5.6 mmol) $HgCl_2$). Two recrystallizations from dichloromethane–ethanol yielded pure **2** (2.31 g, 64%). Data for **2**: m.p. 108 °C; IR (nujol mull, cm^{-1}) 3086, 1543, 1260, 1223, 1197, 1087, 1019, 994, 963, 918, 883, 771, 709, 691, 659, 633, 581, 527, 448, ^{1}H NMR ($CDCl_3$, δ in ppm, J in Hz, TMS at $\delta = 0$) 7.10 (dd, 1H, $J = 2.45$, C*H*), 6.78 (dd, 1H, $J = 1.75$, C*H*), 6.40 (dd, 1H, $J = 1.00$, C*H*), 5.25 (s, 1H, 0.5 CH_2Cl_2), 1.13 (d, 18H, $^3J_{HH} = 7.48$, Si[CH(CH_3)$_2$]$_3$), 1.49 (sept, 3H, $^3J_{HH} = 7.50$, Si[C*H*(CH$_3$)$_2$]$_3$). ^{13}C NMR ($CDCl_3$, δ in ppm, TMS at $\delta = 0$) 148.2 (s, *C*Hg), 131.5 (s, CH), 124.5 (s, CH), 117.2 (s, Si[*C*H(CH$_3$)$_2$]$_3$), 17.9 (s, Si[CH(*C*H$_3$)$_2$]$_3$), 11.8 (Si[*C*H(CH$_3$)$_2$]$_3$). Anal. Found: C, 46.21; H, 7.27; N, 3.83. $C_{26}H_{48}HgN_2Si_2 \cdot 1/2CH_2Cl_2$. Calc: C, 46.23; H, 7.18; N, 4.07%. MS: m/z 646 (M^+).

It is also possible to obtain the monosubstituted mercury compound **1** from **2** through reaction of **2** with an equivalent amount of mercuric chloride. Cleavage of the triisopropylsilyl group from compound **2** is easily achieved through reaction with tetra(n-butyl)ammonium fluoride to give $(3\text{-}C_4H_3NH)_2Hg$ (**3**) [6].

$(3\text{-}C_4H_3NH)_2Hg$ (**3**) was prepared in the following way: a solution of tetra(n-butyl)ammonium fluoride · $3H_2O$ (444 mg, 1.4 mmol) in tetrahydrofuran (4 ml) was added dropwise to a solution of **2** (454 mg, 0.7 mmol) in the same solvent (2 ml). After 10 min at room temperature dichloromethane and water was added to the reaction mixture. The dichloromethane phase was separated and the solvent removed under vacuum. Three recrystallizations of this material from dichloromethane–hexane afforded pure **3** (112 mg, 48%). Data for **3**: m.p. 240 °C (decomposition); IR (nujol mull, cm^{-1}) 3351 (νNH), 3091, 1506, 1260, 1132, 1073, 1055, 905, 886, 858, 779, 733, 717, 659, 638, 585, 563, ^{1}H NMR ($CDCl_3$, δ in ppm, TMS at $\delta = 0$) 8.61 (s, 1H, N*H*), 7.12 (s, 1H, C*H*), 6.81 (s, 1H, C*H*), 6.34 (s, 1H, C*H*), 5.27 (s, 2H, CH_2Cl_2 of crystallization); ^{13}C NMR ($CDCl_3$, δ in ppm, TMS at $\delta = 0$) 125.0 (s, *C*H), 118.3 (s, *C*H), 115.5 (s, *C*H), (quaternary C resonance not observed). Anal. Found: C, 26.00; H, 2.01; N, 7.18. $C_8H_8HgN_2 \cdot CH_2Cl_2$. Calc: C, 25.88; H, 2.41; N, 6.71%. MS: m/z 334 (M^+).

Confirmation that mercuration has occurred in the 3-position of compounds **1**–**3** was provided by the NMR and IR data and by a crystal structure determination of **1** (Fig. 1). X-ray crystal structure analysis data: $C_{13}H_{24}ClHgNSi$, $M_r = 458.46$ g mol^{-1}, orthorhombic, space group *Pbcn*, $a = 16.223(2)$, $b = 16.112(2)$, $c = 12.741(5)$ Å, $V = 3330.3(12)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.829$ g cm^{-3}, crystal size $0.42 \times 0.22 \times 0.22$ mm^3, 25 reflections for lattice parameters ($22 \leq 2\theta \leq 29°$), $T = 193$ K, $\mu_{calcd} = 9.45$ mm^{-1}, $F(000) = 1760$. Data collection and correction: Enraf Nonius CAD-4 diffractometer, Mo Kα radiation, graphite monochromator, ω–2θ scan ($1.8 \leq 2\theta \leq 25.0°$), hkl boundaries $0 \leq h \leq 19$, $-19 \leq k \leq 0$, $0 \leq l \leq 15$, 2924 unique reflections, 1969 observed reflections with $F_o > 4\sigma(F_o)$, corrections: psi scan. Solution and refinement: structure solution by Patterson method, full-matrix least squares refinement, 236 parameters refined. All hydrogen posi-

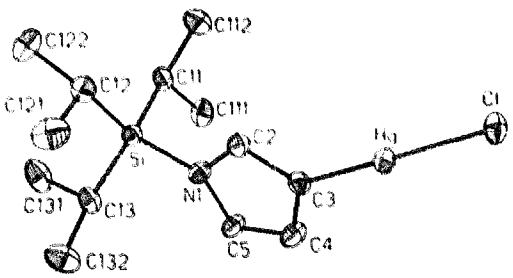
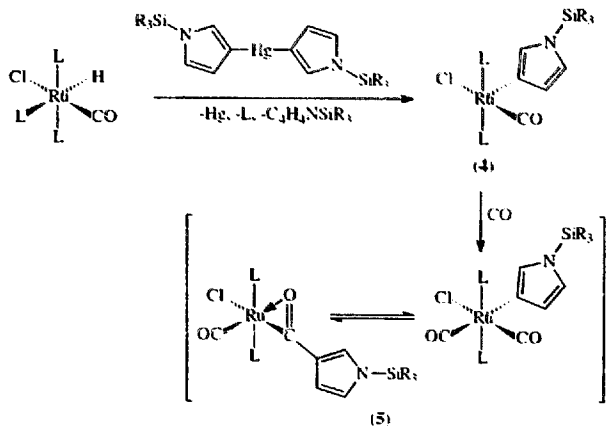


Fig. 1. Molecular structure of (3-$C_4H_3NSi[CH(CH_3)_2]_3$)HgCl (**1**). Hg–C3 2.007, Hg–Cl 2.324, N1–C2 1.385, N1–C5 1.387, N1–Si 1.775 Å; C3–Hg–Cl 177.9°.



[L = PPh_3, R = $CH(CH_3)_2$]

Scheme 2.

tions were refined; final residue values: $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.029$, $wR_2 = \{\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2\}^{1/2} = 0.066$, GooF = $\{\Sigma w(F_o^2 - F_c^2)^2/(n-p)\}^{1/2} = 1.05$, $\Delta\rho$(max./min.) = 0.66/−0.89 e Å^{-3}. All refinements were performed by using the SHELXL-93 program system [7]. Full details of the crystal structure investigation will be sent to the Cambridge Crystallographic Data Centre. These may be obtained from the Director, Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, on quoting the full journal citation.

The protected bis(pyrrolyl)mercury **2** reacts with $RuHCl(CO)(PPh_3)_3$ to give the red, five-coordinate compound **4** (see Scheme 2). Addition of CO to a dichloromethane solution of **4** gives the dicarbonyl complex **5** which exists in equilibrium with the corresponding η^2-acyl, monocarbonyl complex.

$RuHCl(CO)(PPh_3)_3$ (185 mg, 0.19 mmol) and **3** (140 mg, 0.22 mmol) were dissolved in dry, degassed benzene (30 ml) and heated at reflux under nitrogen for 15 min. The resulting red solution (which contains **4**) was allowed to cool to room temperature. CO was bubbled through the solution causing it to become yellow. A yellow solid was isolated from this solution in the usual way. Recrystallization of this solid from dichloromethane–ethanol yields pure **5** (142 mg, 78%). Data for **5**: m.p. 176°C. IR (nujol mull, cm^{-1}) 3059, 1908, 1542, 1510, 1260, 1209, 1189, 1096, 847, 751, 729, 694, 587, 517. ^{1}H NMR ($CDCl_3$, δ in ppm, J in Hz, TMS at $\delta = 0$) 7.6–7.2 (m, 30H, PPh_3), 6.63 (s, acyl), 6.17 (s, acyl), 6.12 (s, acyl), 6.60 (s, dicarbonyl), 5.90 (s, dicarbonyl), 5.80 (s, dicarbonyl) pyrrole-CH (integrating in total to 3H): 5.25 (s, 2H, CH_2Cl_2), 1.24 (sept, 3H, $Si[CH(CH_3)_2]_3$), 0.96 (d, 18H, $J_{HH} = 7.08$, $Si[CH(CH_3)_2]_3$). ^{13}C NMR ($CDCl_3$, δ in ppm, TMS at $\delta = 0$) 134.7 (s, *meta-C*, PPh_3, dicarbonyl), 134.4 (s, *meta-C*, PPh_3, acyl), 132.1 (s, *ipso-C*, PPh_3), 129.8 (s, *para-C*, PPh_3), 127.9 (s, *ortho-C*, PPh_3, acyl), 127.6 (s, *ortho-C*, PPh_3, dicarbonyl), 18.0 (s, $Si[CH(CH_3)_2]_3$, dicarbonyl), 17.6 (s, $Si[CH(CH_3)_2]_3$, acyl), 11.7 (s, $Si[CH(CH_3)_2]_3$, dicarbonyl), 11.2 (s, $Si[CH(CH_3)_2]_3$, acyl) (pyrrole-C are not observed). ^{31}P NMR ($CDCl_3$, δ in ppm, 85% H_3PO_4 at $\delta = 0$) 32.7 (acyl), 17.7 (dicarbonyl). The above assignments to either the 'dicarbonyl' or 'acyl' form are tentative. Anal. Found: C, 60.97; H, 5.65; N, 1.31. $C_{51}H_{54}ClNO_2P_2RuSi \cdot 1CH_2Cl_2$. Calc: C, 60.96; H, 5.51; N, 1.37%. MS: m/z 904 ($M^+ - Cl$). Note: we have not yet obtained **4** in an analytically pure form.

Crystallization with ethanol produces **5** exclusively in the acyl form (ν(CO) = 1908 cm^{-1}), whereas in solution the dicarbonyl and the acyl forms coexist as shown by IR bands at 2038, 1968 cm^{-1} and 1908 cm^{-1} respectively. The relative intensity of the carbonyl bands in a chloroform solution indicates that approximately equal amounts of the dicarbonyl and acyl forms are present; similar behaviour has been observed for related σ-aryl complexes of ruthenium [8].

The use of the deprotected bis(3-pyrrolyl)mercury (**3**) as a 3-pyrrolyl transfer agent towards ruthenium and osmium is currently being explored.

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